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SPECTRA OF PRESSED DISKS OF ALKALI HALIDE WHISKER CRYSTALS INCO--ETC(U)
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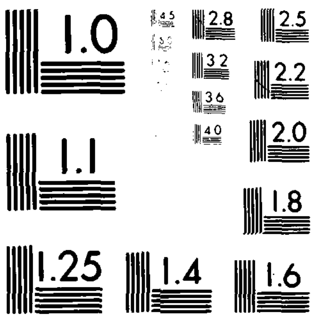

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LEVEL II

6 Spectra of Pressed Disks of Alkali Halide Whisker Crystals Incorporating Foreign Ions.

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by

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and

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FOREWORD

This report describes a method for the growth of whisker crystals of ionic compounds and for obtaining spectra of foreign ions incorporated in alkali halides without the necessity of growing large single crystals. The work was funded under Task area ZR02402.

This report was reviewed for technical accuracy by William R. McBride.

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(U) *Spectra of Pressed Disks of Alkali Halide Whisker Crystals Incorporating Foreign Ions*, by Marian E. Hills and Allen L. Olsen. China Lake, Calif., Naval Weapons Center, April 1980. 12 pp. (NWC TP 6185, publication UNCLASSIFIED.)

~~(U)~~ Alkali halide whisker crystals of KCl, KBr, KI, and NaCl were grown readily by allowing aqueous solutions of the salts to pass through porous glass. Whisker crystals of alkali halides doped with MnO_4^-, ClO_4^-, and ClO_3^- were also grown; not all dopants were used with all host lattices. The whisker crystals may be pressed into disks suitable for obtaining optical spectra. The absorption bands in the spectra of disks pressed from doped whisker crystals were sharper than the spectra of disks pressed from a mechanical mixture of the alkali halide and the dopant. The versatility of the porous glass technique for the growth of whisker crystals is clearly demonstrated.

MnO4(-), ClO4(-) and ClO3(-)

2

The feed solutions were unsaturated aqueous solutions of the alkali halides, either pure or containing small amounts of the ion of interest. The composition of the pure solutions employed is shown in Table 1.

TABLE 1. Composition of Pure Alkali Halide Feed Solutions.

Salt	Grams of salt/ 100 grams solution	Percent of saturation at 20°C
NaCl	20	76
KCl	19	76
KBr	32	82
KI	40	68

The whisker crystals were pressed into disks 7/8-inch in diameter under vacuum and at a pressure of 133,000 psi.[5] Some whisker crystals were pressed into disks in the condition in which they were harvested and some were broken up by vibrating them together with three 5/32-inch steel balls in a capsule for one minute.

The infrared spectra were run on a Perkin-Elmer Model 137, 221, or 621 spectrophotometer and the ultraviolet and visible spectra on a Perkin-Elmer Model 202 or a Cary Model 14R spectrophotometer.

RESULTS AND DISCUSSION

Alkali halide whisker crystals grow readily on porous glass, particularly silicone rubber coated porous glass (Figure 2). The formation on a porous glass tube of a whisker-crystal covering a centimeter thick in 24 hours is not unusual.

A photomicrograph of alkali halide whiskers is shown in Figure 3. The visual clarity (transmission) of pressed disks of alkali halide whiskers is shown in Figure 4. The photographs of the disks were taken shortly after they were pressed and indicate that better quality disks can be obtained from broken whiskers (those shaken with steel balls) than can be obtained from unbroken whiskers. The ultraviolet spectra of disks of pressed whiskers show good transmission into the ultraviolet region; the ultraviolet spectrum of a potassium bromide disk is shown in Figure 5.

[5] Allen L. Olsen. "Potassium Bromide Pellet Technique," *Anal. Chem.*, Vol. 31, No. 2 (February 1956), pp. 321-22.

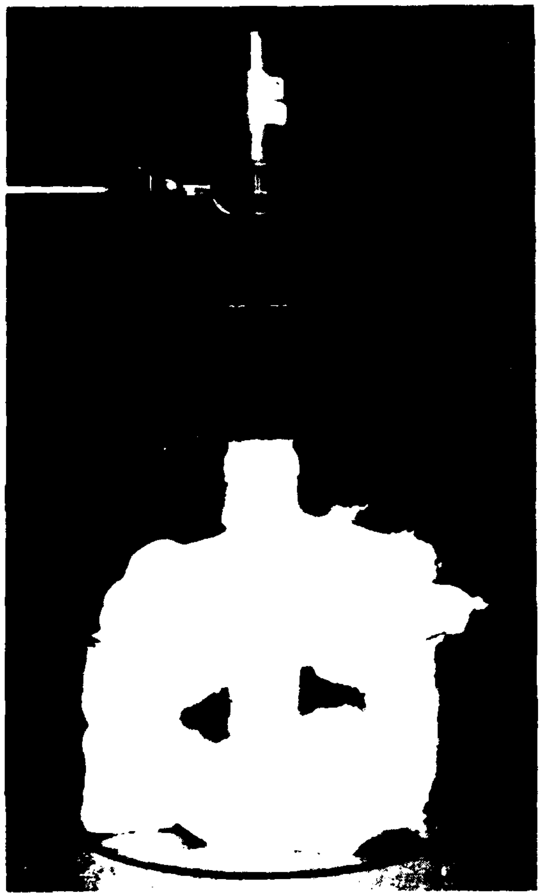

FIGURE 2. Whisker Crystals of Potassium Bromide Growing on Tube Shown in Figure 1.

FIGURE 3. Photomicrograph of Potassium Bromide Whiskers. The magnification is about 160X, which corresponds to 6.25 μm/mm.

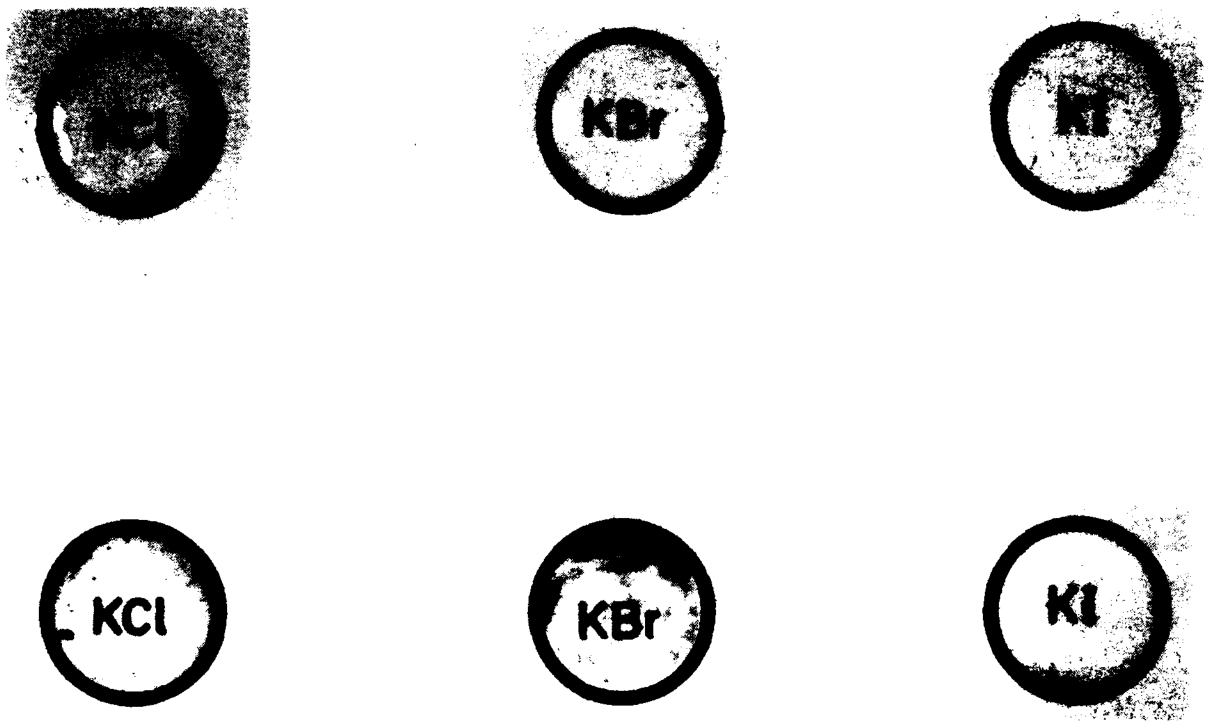

FIGURE 4. Pressed Disks of Alkali Halide Whiskers. Disks shown in the upper row were pressed from whiskers broken with steel balls prior to pressing. These disks show greater clarity than those pressed from unbroken whiskers (bottom row).

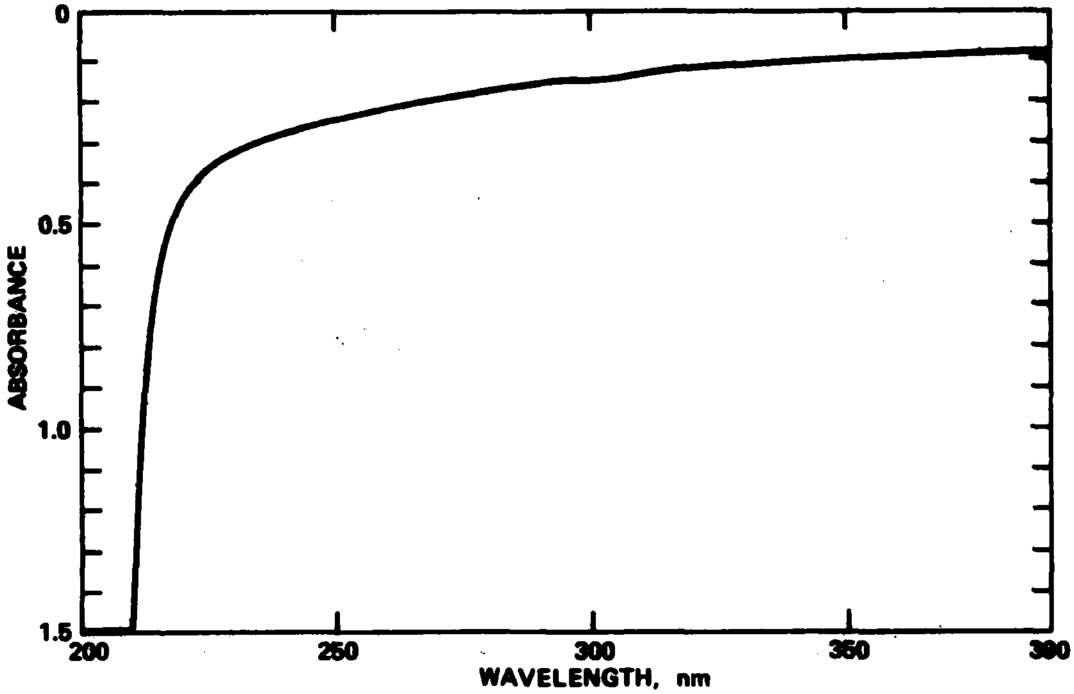

FIGURE 5. Ultraviolet Spectrum of a Disk Pressed From Potassium Bromide Whiskers.

Whisker crystals were grown from various alkali halide solutions containing small amounts of permanganate, perchlorate, chlorate, sulfate, chromate, dichromate, lead, or ammonium ions. Sharp absorption bands in the spectra of pressed disks were found which could be associated with permanganate, perchlorate, or chlorate ions. The infrared spectra for these are shown in Figures 6-8. For purposes of comparison spectra are also shown for disks pressed from a physical mixture of Harshaw KBr powder and small quantities of potassium permanganate, potassium perchlorate, or potassium chlorate. Figure 9 shows the spectra of perchlorate ion in potassium chloride, potassium bromide, and potassium iodide.

The spectrum for perchlorate agrees with that obtained by Hisatsune and Linnehan[6] after they had heated pressed disks of ClO_4^-:KCl to change the broad band near 1120 cm^{-1} to a pair of sharp bands at 1133 and 1119 cm^{-1} for use in their study of the kinetics of the decomposition of the perchlorate ion.

[6] I. C. Hisatsune and D. G. Linnehan. "Thermal Decomposition of the Perchlorate Ion in a Potassium Chloride Matrix," *J. Phys. Chem.*, Vol. 74, No. 23 (1970), pp. 4091-95.

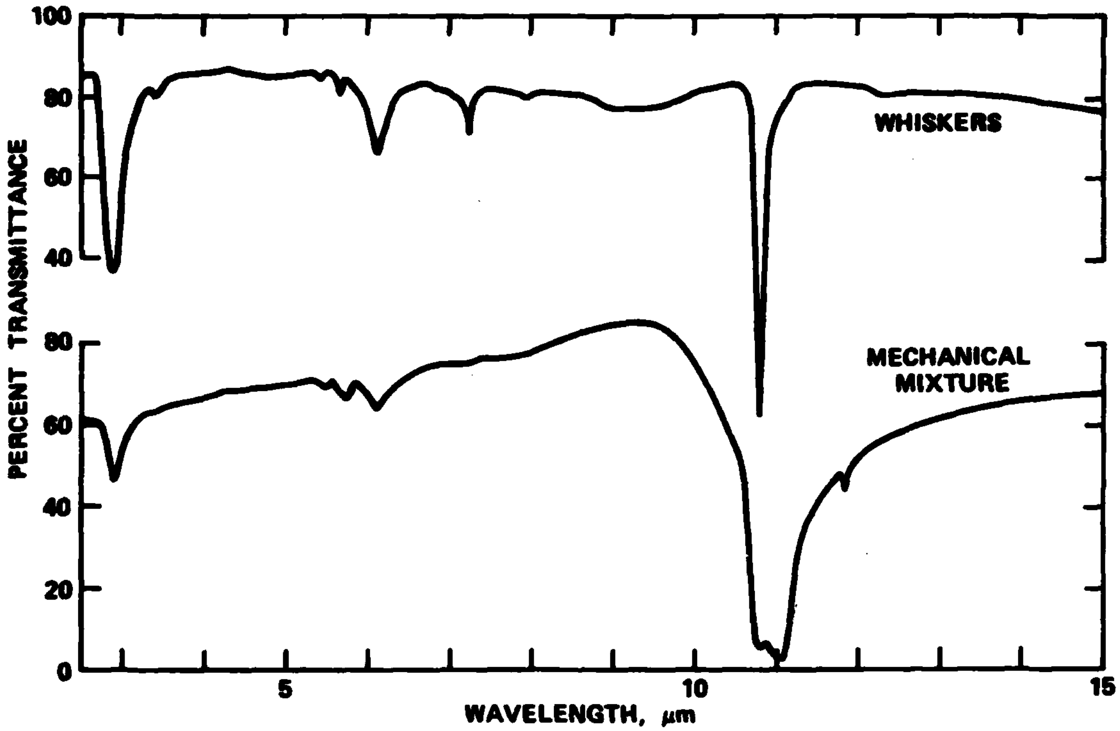

FIGURE 6. Infrared Spectra of Pressed Disks. Upper Curve: Potassium bromide whiskers grown from solution containing a small amount of potassium permanganate. Lower Curve: Mechanical mixture of Harshaw potassium bromide powder and a small amount of potassium permanganate.

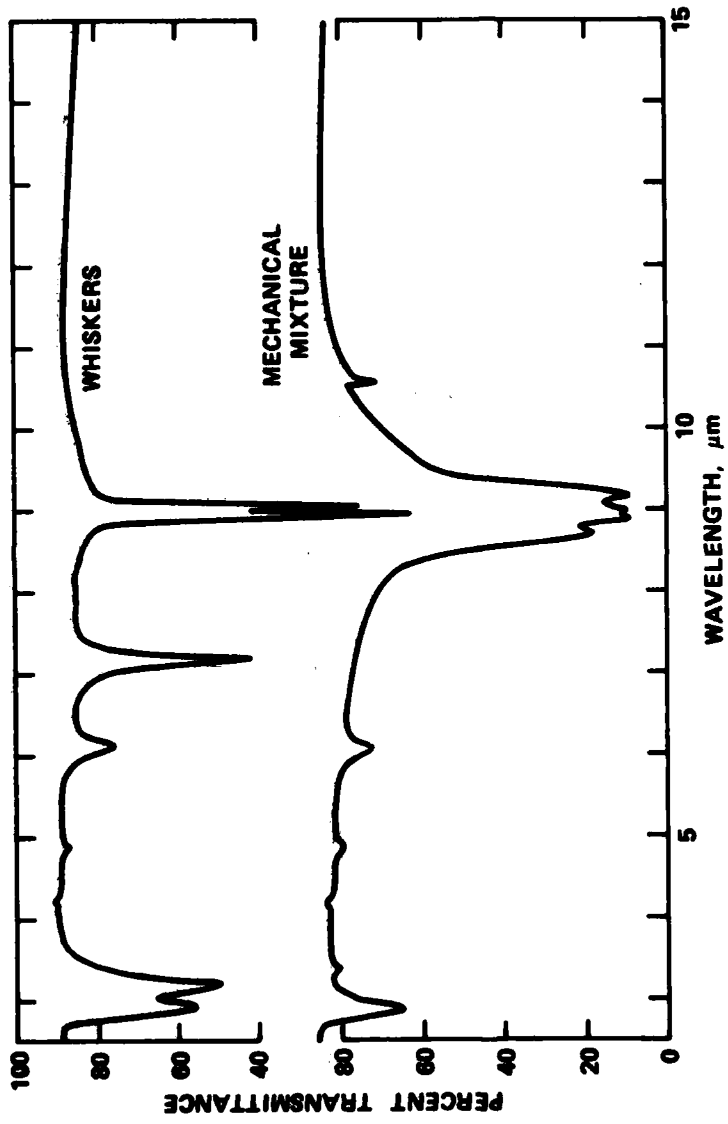

FIGURE 7. Infrared Spectra of Pressed Disks. Upper Curve: Potassium bromide whiskers grown from solution containing a small amount of potassium perchlorate. Lower Curve: Mechanical mixture of Harshaw potassium bromide powder and a small amount of potassium perchlorate.

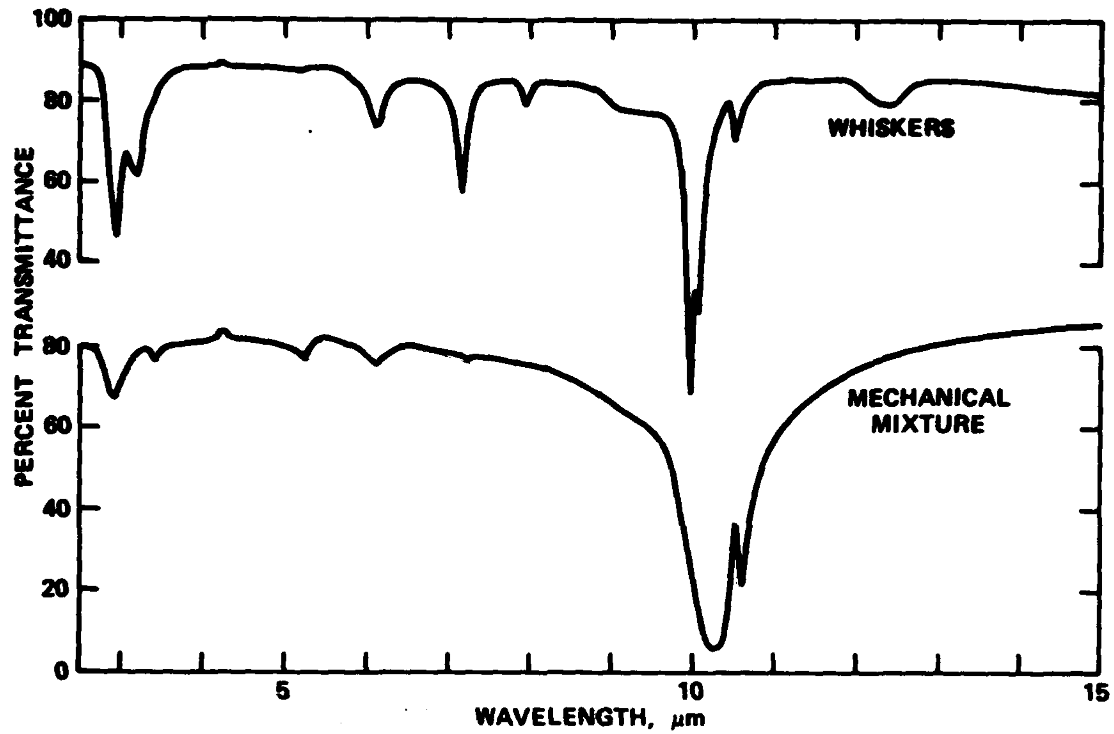

FIGURE 8. Infrared Spectra of Pressed Disks. Upper Curve: Potassium bromide whiskers grown from solution containing a small amount of potassium chlorate. (Growth tube may have been slightly contaminated with ammonium ions.) Lower Curve: Mechanical mixture of Harshaw potassium bromide powder and a small amount of potassium chlorate.

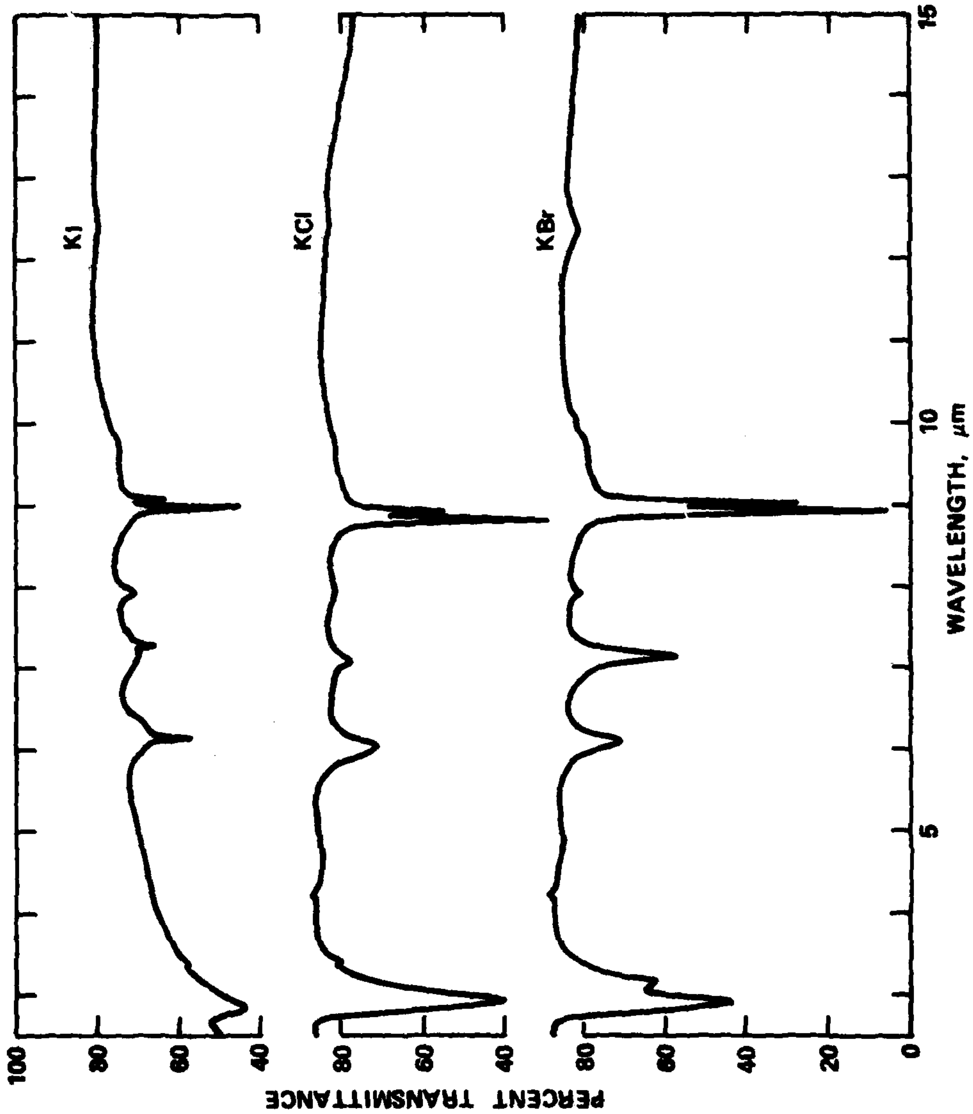

FIGURE 9. Infrared Spectra of Pressed Disks of Whisker Crystals Grown From Solutions Containing Small Amounts of Potassium Perchlorate.

Some KBr from the same supply used to make feed solutions was ground by hand in an agate mortar, sieved (particle sizes ranged from 44 μm to 74 μm), and pressed into a disk; its IR spectrum showed some bands. Heating the KBr near its melting point or fusion before grinding and pressing resulted in the reduction of some of the impurity bands. The extent of impurity bands in pressed KBr disks varied from bottle to bottle of material used to prepare feed solutions, even for the same manufacturer. Since some impurity bands appeared both in disks pressed from the bulk KBr and whisker KBr, it appears that recrystallization at room temperature did not remove the source(s) of all the impurity bands.

X-ray measurements of a few of the KBr whiskers showed that they had grown in the <100> direction. This is the same as the reported behavior for KBr[7] grown on cellophane.

Whiskers were grown from aqueous KCl-KBr solutions. X-ray diffraction patterns showed that the whiskers were mixed crystals and not a mechanical mixture of KCl whiskers and KBr whiskers. Solubility data show that potassium chloride and potassium bromide form a completely miscible system at room temperature. Attempts to press KCl-KBr whiskers into disks were not successful; the disks cracked in a radial pattern.

CONCLUSIONS

For some ionic compounds whisker crystals can be grown readily from porous glass in such quantities as to make them useful for pressed pellet work. The pellets may be used:

1. To obtain spectra of ions in various crystal lattices.

2. To obtain some indication of the solubility of ions in various lattices by optical means without the necessity to grow large single crystals of the material.

3. To obtain specimens for use in kinetics studies.

ACKNOWLEDGMENT

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[7] B. E. Powell and Byron M. McKibben. "Alkali-Halide Filamentary Crystals," *J. Cryst. Growth*, Vol. 8 (1971), pp. 276-78.

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